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Measurements of Light Extinction by Single Aerosol Particles

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ABSTRACT. A Bessel beam optical trap is combined with continuous wave cavity ringdown spectroscopy to measure the extinction cross-section of individual aerosol particles. Particles, ~ 1 μm in size, can be captured indefinitely and processes that transform size or refractive index studied. The measured extinction induced by the particle is shown to depend on the position of the particle in the cavity, allowing accurate measurements of the mode structure of a high finesse optical cavity without significant perturbation. The variation in extinction efficiency of a sodium chloride droplet with relative humidity is shown to agree well with predictions from Mie scattering theory.

Elastic light scattering is widely used as a tool to interrogate the size distributions, morphologies and refractive indices of particles in colloidal dispersions. Measurements are made of the variation in light intensity with scattering angle,¹⁻² the attenuation of intensity when passed through a sample³ or of the transient peak in scattered intensity.⁴ Although measurements in the near forward and backward scattering geometries are desirable, providing the greatest sensitivity to particle size and allowing direct measurements of quantities such as the extinction efficiency, such measurements are mostly overwhelmed by the direct transmission of light through the sample without interaction. Light extinction, scattering and absorption efficiencies are, however, key quantities that can be directly compared with predictions from Mie's solution to Maxwell's equations when considering light scattering by a sphere or solutions from, for example, the T-matrix method when considering nonspherical particles.⁵ An improved understanding of the optical properties of particles is critical for better describing light scattering and absorption by aerosol particles and their impact on the radiative balance of the atmosphere and climate change.⁶ Moreover, any opportunity to monitor the variation in optical properties of a single particle with change in environmental conditions such as relative humidity (RH) would provide invaluable data for constraining and improving the description of the interaction of light with ambient particles. Further, unambiguous measurement on single particles would be uncomplicated by dispersion in particle shape, composition and morphology.

Cavity ringdown spectroscopy (CRDS) has proven to be a sensitive tool for measuring the extinction efficiency of ensembles of aerosol particles.^{5, 7-8} Measurements are typically made on a number of selected particle sizes at a single or multiple wavelengths. Each size-resolved measurement is inevitably derived from a sample of narrow but finite size distribution, possibly

even containing a small number of much larger particles of identical electrical mobility when selected by a differential mobility analyser.⁹ Comparative measurements of change in optical extinction with change in environmental conditions (e.g. RH) are often more reliable than attempts to make a single absolute measurement of the optical cross-section.¹⁰⁻¹¹ Despite these complications, CRDS has been used to investigate particles of complex morphology (e.g. mineral dust and core-shell particles),¹²⁻¹⁴ the optical growth factor with increasing RH,¹⁰ and the single scattering albedo of light absorbing aerosol.¹⁵ We report here a new approach for measuring absolute light extinction by *single* aerosol particles captured within a Bessel beam optical trap over an extended time frame, removing the ambiguities that are often associated with ensemble measurements and allowing direct determination of the change in optical properties of sub-micrometre sized aerosol particles over time.

A zeroth order Bessel beam (BB) can be described as a pseudo non-diffracting beam formed experimentally by the interference of an infinite series of plane waves propagating with wavevectors that lie on the surface of a cone, forming an on-axis intense core surrounded by many rings that convey equal power (Figure 1).⁵ We have shown that aerosol particles (1.5 to 5 μm diameter) can be captured within a Bessel beam of core diameter 7 μm and guided along the propagation axis z over a distance approaching 1 cm.¹⁶⁻¹⁷ A degree of selection over particle size can be achieved through judicious choice of core diameter and power, allowing the manipulation of particles from <500 nm to >10 μm radius. The light intensity varies along the axial direction with the peak intensity towards the centre of the propagation distance, z_{max} .¹⁸ Particles that are confined radially through the gradient force within a vertically propagating BB adopt an axial z -position (height) at which the radiation pressure (the optical force), gravitational force and drag

force (in the presence of a gas phase flow) balance. The variation in the optical force with particle size varies in a complex way that can be estimated from the radiation pressure efficiency calculated from Mie theory for spherical particles.^{5, 19} The vertical displacement of a trapped droplet can be held constant by varying the intensity of light in the central core through control of the laser power, comparable to the approach used in simple Gaussian beam levitation traps.²⁰

Radiation pressure measurements made with evaporating 1,2,6-hexanetriol droplets are shown in Figure 2(a), reporting the variation in laser power with time required to hold the droplet at a fixed height as a droplet evaporates and the size changes. The measurements are compared with estimates of the relative change in light intensity expected based on the size dependence of the radiation pressure efficiency and geometric cross-section. The figure illustrates the high degree of reproducibility in the radiation pressure measurements that is observed. The droplet size is estimated from the phase function, the angular variation in the intensity of light scattering from the trapping beam.¹⁷ Figure 2(b) illustrates the level of reproducibility that can be achieved between measurements of the vapour pressure of the evaporating organic aerosol, even down to particles smaller than 500 nm radius. Evaporation is driven by diffusional mass transport into a gas phase of flowing pure nitrogen gas, which continually displaces evaporated 1,2,6-hexanetriol from the trapping cell and keeps the partial pressure of the evaporating component close to 0 Pa. From the evaporation rate, the vapour pressure can be estimated and the average value from these measurements is $(4.41 \pm 0.67) \times 10^{-4}$ Pa; we are unable to find a previously reported value for comparison.

Here, we use continuous wave CRDS to make measurements of optical extinction; references 13 and 21 provide a comprehensive overview of the approach and the differences from pulsed CRDS. With the BB propagating vertically, an axis for the CRDS is established in the horizontal plane (Figure 1). A small fraction of the laser power used to form the BB is separated by a polarising beam splitter cube and gently focussed through an acousto-optic deflector, which deflects the incoming beam away from the input mirror following cavity build-up to trigger a ringdown event. The 0.5 m long optical cavity for cw-CRDS is formed by two highly reflective mirrors (>99.99 % reflectivity at 532 nm, Layertec). One of the mirrors is mounted on a piezo ring actuator (Piezomechanik), which translates the mirror along the axis of the cavity, periodically sweeping the cavity into resonance with the laser. A 750 mm focal length lens is used to match the incoming beam with the desired TEM₀₀ mode of the optical cavity. The time constant for the empty cavity is typically $20.00 \pm 0.35 \mu\text{s}$.

The sensitivity of particle height to laser power in the Bessel beam core can readily allow the translation of the particle over distances of a millimetre or more. In Figure 2 we have shown that we can stabilize a trapped particle at a fixed height (z -position in the CRD beam) even when the particle is changing size; here, we vary the Bessel beam trapping power to control actively the position of the particle along the z -axis. When performing CRDS, such control over particle position has an important benefit: the particle can be moved in and out of the CRD beam almost instantaneously, allowing accurate and sequential measurements of the ringdown time both with (τ) and without (τ_0) the particle present in the cavity.

The variation in ringdown time with the position of a particle within the CRD beam is shown in Figure 3. Not only can the particle be translated vertically along the z -axis by varying the laser power in the BB, but also along the y -axis (orthogonal to the cavity axis) by translating the position of the final mirror in the BB arrangement (Figure 1). The measurements shown in Figure 3 illustrate the sensitivity in the ringdown time to the position of the particle within the Gaussian waist of the beam (y, z), with the largest reduction observed only when the particle is carefully aligned to the centre of the TEM₀₀ mode profile. The dimensionless light extinction per pass through the cavity, $\varepsilon(y, z)$, induced by the single aerosol particle can be calculated if the change in ringdown time and cavity length, L , are known:²²

$$\frac{1}{\tau} - \frac{1}{\tau_0} = \frac{\varepsilon(y, z)c}{L} \quad (1)$$

The extinction per pass can be related to the extinction cross-section for the particle, σ_{ext} , and the local intensity of light in the cavity at the position of the particle, $i(y, z)$,

$$\varepsilon(y, z) = \frac{\sigma_{ext} i(y, z)}{I} \quad (2)$$

where I is the total intensity in the CRD beam. The Gaussian intensity profile of the CRD beam can be written as

$$i(y, z) = \frac{2I}{\pi w^2} e^{-2(y^2 + z^2)/w^2} \quad (3)$$

where the centre of the Gaussian profile is $y = z = 0$ and the beam waist is w . Thus, from Figure 3, the full-width at half maximum of the CRD beam at the exact centre of the cavity can be measured as $386 \pm 12 \mu\text{m}$, similar in dimension to that estimated from the focal lengths of the mirrors for the cavity, $319 \mu\text{m}$. The reason for the discrepancy is not clear at this stage. The contribution of higher order modes in the CRD signal can be ruled out with some confidence: the

mode profile leaving the cavity is routinely imaged by a camera and only ringdown events from excitation of a TEM_{00} are selected and analysed. We cannot be certain that the BB trap is located exactly at the midpoint of the cavity, but the beam waist can be estimated to increase to only 368 μm at the mirrors.

The measurement presented in Figure 3 provides a unique and direct method for investigating the standing wave formed within the optical cavity; while a macroscopic probe unavoidably prevents the mode from becoming established, the insertion of a microscopic probe particle allows the light intensity within the cavity to be inferred. With the experimental configuration shown in Figure 1, it was not possible to translate the particle along the x -axis, i.e. from peak to node along the standing wave of the CRD beam. The particle sizes considered here are typically at least a factor of two larger than the wavelength used in the CRD measurement and confinement of the particles laterally in the trap can be estimated to be better than $\pm 1.6 \mu\text{m}$ from the brightfield images. Although the apparent extinction cross-section measured is expected to depend on the position of the particle relative to the standing wave pattern of the CRD beam based on theoretical calculations by Miller et al.,²³ it is anticipated that this can lead to an error of at most 10 % in the extinction measurement over the radius range 800 to 1200 nm, depending on the exact droplet size.

By independent control of the (y,z) position of the particle when held within the BB trap, the particle can be moved to the point of highest light intensity where it leads to the greatest depression in the cavity ringdown time. The particle is then held fixed at this point in the

brightfield image by actively tracking any change in radiation pressure by altering the laser power. All subsequent measurements are performed at this position, where the local intensity is:

$$i(0,0) = \frac{2I}{\pi w^2} \quad (4)$$

Then, the change in ringdown time can be related to the extinction cross-section of the particle:

$$\frac{1}{\tau} - \frac{1}{\tau_0} = \frac{2c\sigma_{ext}}{L\pi w^2} \quad (5)$$

An example of the change in ringdown time for an aqueous sodium chloride droplet with variation in relative humidity (RH) is shown in Figure 4(a) along with the variation in droplet size. The aerosol droplet was initially captured at an RH of 90 % from a medical nebuliser and the change in extinction cross-section monitored by CRDS over a timescale of ~5000 s as the RH was allowed to decline steadily to the efflorescence RH of 45 %. The radius of the droplet was measured by elastic light scattering concurrently with the ringdown time measurements. The value of τ_0 was determined at the beginning and end of the experiment and no systematic drift in the value was observed over the timescale of the experiment. The droplet size was measured with a time resolution of 1 s and the ringdown time at ~10 Hz.

Structure in the extinction cross-section is apparent even from the raw ringdown times presented in Figure 4(a). The envelope of scatter in ringdown times is dependent on fluctuations in particle position (x , y and z), the inherent noise in ringdown time and the challenges of making extinction measurements when the droplet size is resonant with the laser wavelength, which can lead to large excursions and perturbations in particle position. The variation in the retrieved extinction efficiency is compared with calculations from Mie theory in Figure 4(b), including the variation in refractive index with RH/solute concentration and, thus, droplet size. The refractive index is

expressed on a molarity scale taken from the partial molal refractions and densities for aqueous sodium chloride solutions in reference 24, with the composition and refractive index then scaling with droplet volume. For comparison, a Mie calculation with fixed refractive index is shown. The agreement between the measured and calculated extinction efficiencies is excellent, provided the variation in refractive index is correctly treated, with the Mie calculations reproducing the measured trend within the two standard deviations in fluctuation in CRD time.

From the empty cavity ringdown time quoted earlier ($20.00 \pm 0.35 \mu\text{s}$), the sensitivity of the instrument can be estimated as 1.45×10^{-6} and the variation in ringdown time with particle size can be estimated. A particle of radius ~ 200 nm and refractive index 1.33 would yield a ringdown time of $19.65 \mu\text{s}$, clearly indicating that even with this instrument it should be possible to record extinction efficiency curves for single particles well into the accumulation mode size regime. It should be noted, however, that manipulating particles in the accumulation mode will become more difficult as the radiation pressure efficiency decreases progressively with diminishing particle radius. We estimate that a power of 170 mW in the core will be required to capture a particle of 200 nm radius. By reducing the cross-section of the BB core and increasing the power, however, it will be possible to record the extinction cross-section of a ~ 200 nm radius particle with the CRD instrument as described.

In conclusion, we have presented a novel approach to measure light extinction by a single particle captured in a BB trap and probed by CRDS. We have shown that elastic light scattering and radiation pressure measurements can be used to probe aerosol transformation, such as the dynamics of evaporation, over extended timescales for particles smaller than 500 nm radius.

CRD measurements have quantified the change in optical cross-section for an aqueous sodium chloride droplet with change in RH, and the extinction efficiency has been retrieved and compared with calculations. This approach should allow determination of the evolving optical properties of aerosol over extended periods during chemical or physical transformation.

FIGURES

Figure 1. Schematic diagram of the single aerosol particle CRDS instrument. The Bessel beam profile is shown with brightfield and elastic scattered light images from an optically trapped droplet.

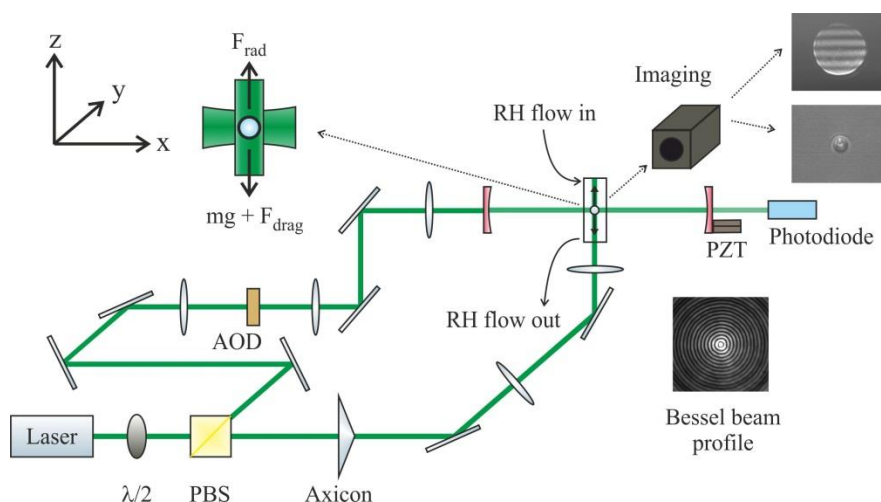


Figure 2. (a) The measured trapping power required to hold an evaporating hexanetriol droplet at a fixed vertical position in the BB. Three experiments are shown along with a simulated trend in the trapping power (dashed line). (b) The change in measured radius over time for five hexanetriol droplets. Inset is an example of the corresponding change in radius squared.

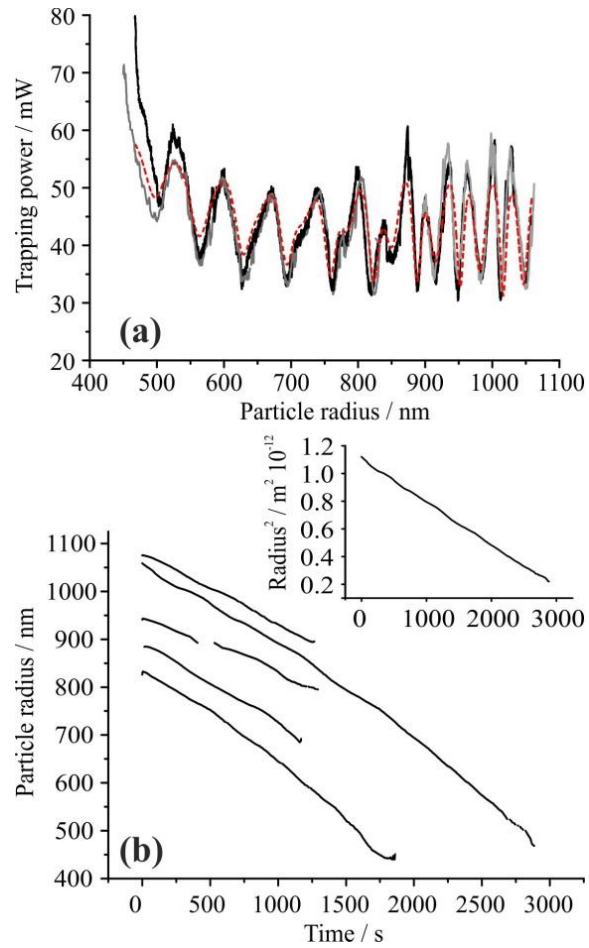


Figure 3. Sensitivity of the measured ringdown time to the position of a 1 μm radius particle within the CRDS beam. The change in ringdown time with vertical position is recorded for a particle passing through the centre of the beam (black symbols) and $\sim 200\text{ }\mu\text{m}$ off-centre (red symbols).

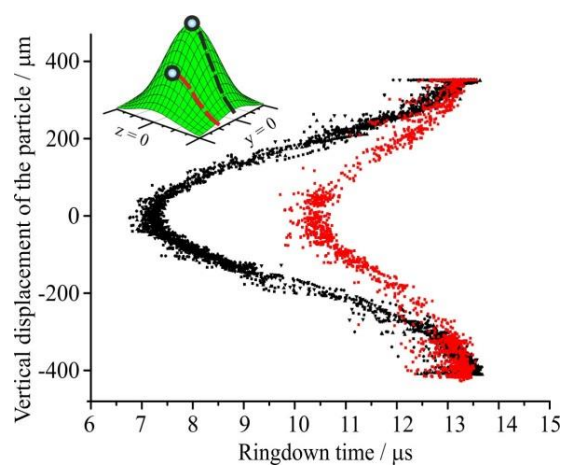
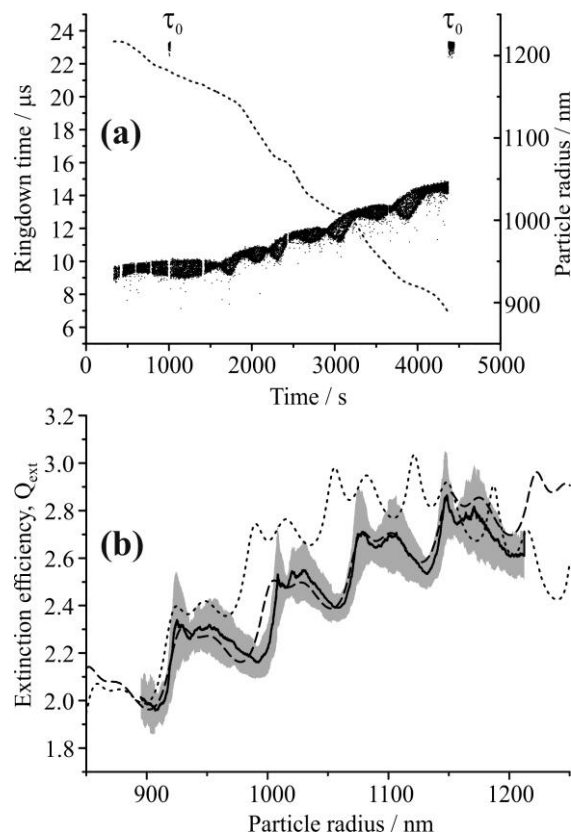


Figure 4. (a) The change in ringdown time for a sodium chloride particle as the surrounding RH and particle radius decrease. (b) The measured (black with grey envelope) and calculated extinction efficiencies for sodium chloride aerosol for which the refractive index is allowed to vary with change in particle radius (long dashed line) and when it is fixed at the value at the smallest size (short dashed line).



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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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